

A CONFIGURATION INTERACTION STUDY
OF THE BERYLLIUM ATOM

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INTRODUCTION

The subject of this work is a study of the ground state of the Be atom by the configuration interaction method, with particular emphasis on the total energy as well as on the quality of the wave function. The techniques used here can be applied quite in general, to the calculation of energy levels, wave functions and related quantities of isolated atoms in their bound states.

The absolute importance of finding these quantities resides in innumerable applications in the field of atomic spectroscopy (energy levels, transition probabilities, hyperfine structure), together with the evaluation of average values giving information on the shape of the electronic cloud, and of all the physical properties of isolated atoms such as, for example, their diamagnetic susceptibility.

The relative importance, however, which is primordial in any growing field, concerns mainly quantum chemistry, where the analysis of accurate wave functions offers: a) an opportunity for testing and improving existing theories on atomic structure and perhaps for suggesting new ones; b) a starting point for better atomic calculations, and c) information useful in molecular calculations, mainly in relation to the search of appropriate basic functions.

Ever since the early days of quantum mechanics, it has been realized that it is almost impossible to solve the electronic Schrödinger equation, and people have concentrated on the computational

point of view, inventing models and finding methods to handle the complicated mathematics involved even in the roughest approximations. It is believed that some intermediate results are necessary in order to make possible the formulation of a many electron theory. It is on these intermediate results that most of the computational work is being done nowadays and ours falls in this category. The Hartree-Fock (HF)⁽¹⁾ and Hartree-Fock-Slater⁽²⁾ calculations on atomic systems are an example, and they are those which have been best studied both theoretically and from the practical point of view.

The HF approximation, or independent particle model, is regarded by many⁽³⁾ as the basis for the understanding of the electronic properties of atomic and molecular systems in their stationary states. One electron properties calculated from good approximations to the HF wave functions are in very good agreement with experiment (there is a theoretical basis to account for this fact⁽⁴⁾). For example, the HF electronic densities agree very well with X-ray results⁽⁵⁾. Much more important, the basis for the modern picture of structural chemistry in terms of cores, shells, bonds and lone pairs, and the treatment of excitation processes lies, to a great extent, in the orbital description of these phenomena. To what extent these pictures remain correct when going to approximations more accurate than HF is one of the interesting problems which concerns the quantum chemists of today⁽⁶⁾.

The idea that molecules are made of atoms which retain much of their individuality after bond formation, is still at the roots of

any molecular theory, and it has been verified by both rigorous and semiempirical calculations (the hydrogen atom being sometimes an exception). The same is true when one considers the removal of one electron to form a closed shell: the structure of the closed shell remains very much the same after ionization of the outer electron.

Thus, the obtaining of very accurate atomic wave functions may be useful to investigate bond formation and the simple and visual models of excitation processes. In this connection, we may mention that presently, there is only one rigorous method to calculate binding energies or the ionization potential of an outer electron: it consists in subtracting, from the energy of the final state (molecular aggregate or ionized atom), the energy of the corresponding initial state. Both quantities are usually so large compared to their difference that the method has been compared to weighing the captain of an ocean liner by taking the difference between the weight of the ship with and without captain. Certainly, the derision of the method does not eliminate the problem, and we are confident that, with the help of the new generation of computers, the present methods of calculation will afford very accurate wave functions and binding energies of small molecules. This will help us to realize better, what the magnitudes of the relevant quantities involved in the existing theory are^(?), as well as to improve the application of it to larger systems.

There are several ways of calculating atomic structures, of various degrees of complexity and accuracy, and which are meant to serve different purposes: ours is to get as close as possible to the

exact wave function. The simplest of all is the configuration interaction (CI) method, or method of superposition of configurations. Its simplicity, together with some pessimistic reports about a convergence failure, has led many to think of it as a "pedestrian approach." The truth is that none of that pessimism is well founded and it reveals mainly the deception of those who have attempted to make use of this method without the right tools.

In this work, we examine, from the practical point of view, some of the well-known difficulties of the method, such as the question of how to select the basic one electron functions and the different configurations. This is treated in Chapters I and II. In Chapter III we consider our calculation step by step. Finally, in Chapter IV we analyze our results.

CHAPTER I

EXPANSION OF THE WAVE FUNCTION

One of the difficult problems in quantum mechanics is to solve the many electron Schrödinger equation

$$H\psi_i = E_i \psi_i \quad (1.1)$$

where H is the many electron Hamiltonian and ψ_i is the wave function of an electronic state with energy E_i .

An expansion of the wave function ψ_i is the starting point for any theory or calculation which concerns Eq. (1.1). The many electron theory of atoms and molecules, as recently developed by Sinanoglu⁽⁷⁾, starts from the so-called cluster expansion, whose advantages are pointed out in Ref. (7): it is a finite expansion for a finite number of electrons and it possesses such a convenient form that each term can be investigated and approximated in the framework of the above mentioned theory; the uniqueness of Sinanoglu's cluster expansion is determined by the HF orbitals of the ground state configuration. Another expansion, the configuration interaction expansion⁽⁸⁾, consists of an infinite sum of determinantal functions (Slater determinants) made up of a complete set of one electron functions, or spin-orbitals. In the CI method, the linear coefficients of the CI expansion

are found by the Ritz variational procedure⁽⁹⁾. Formally, this method is very simple, and, also formally, it can be easily applied to many electron systems; on the other hand, there are some unsolved difficulties with the cluster expansion method in this respect⁽¹⁰⁾. However, by the method of successive partial orthogonalization⁽⁷⁾, any wave function, in particular a CI wave function, can be transformed uniquely into the cluster expansion form and analyzed according to the corresponding many electron theory.

It is very important to stress that all these expansions are, in principle, merely formal⁽¹¹⁾. In order to make use of them, it is indispensable that they converge to the exact solution in a way which is practical from the computational point of view and which is physically meaningful. (From the mathematical point of view, it would be very useful to know something about the real convergence conditions, but unfortunately the problem has only been clarified for the case of two electron systems⁽¹²⁾.)

1.1. Configuration Interaction Expansion

The basic assumption is the existence of an expansion theorem

$$\Psi(x) = \sum_K \Psi_K(x) c_K \quad (1.2)$$

for every normalizable function $\Psi(x)$ of the space-spin coordinate $x=(r,\xi)$ of a single electron, in terms of an orthonormal, complete and discrete set $\{\Psi_K(x)\}$ of one electron functions, or spin-orbitals. For a many electron wave function Ψ , Löwdin applies the same theo-

rem, one coordinate at a time⁽⁸⁾. After introducing the antisymmetrizer (since the electrons are fermions) he obtains:

$$\underline{\psi}(x_1, x_2, \dots, x_N) = \sum_K \psi_K(x_1, x_2, \dots, x_N) c_K \quad (1.3)$$

where

$$\psi_K(x_1, x_2, \dots, x_N) = (N!)^{-\frac{1}{2}} \det \{ \psi_k, \psi_l, \dots \}$$

is a normalized Slater determinant K corresponding to an ordered configuration defined by the set $k < l < m \dots$

The expansion (1.3), without any other symmetry restrictions than to be antisymmetric with respect to exchange of any two space-spin coordinates, allowed Löwdin to treat the convergence problem from a most general point of view⁽⁸⁾. He considered the first order density matrix $\gamma(x_1' | x_1)$

$$\begin{aligned} \gamma(x_1' | x_1) &= N \int \psi^*(x_1', x_2, x_3, \dots, x_N) \psi(x_1, x_2, x_3, \dots, x_N) dx_2 dx_3 \dots dx_N \\ &= \sum_{k,l} \psi_k^*(x_1') \psi_l(x_1) \gamma_{kl} \end{aligned}$$

and observed that the diagonal elements γ_{kk} were given by

$$\gamma_{kk} = \sum_K^{(k)} |c_K|^2$$

where K runs over all configurations containing the specific index k . Then, a new basis $\{\chi_k(x)\}$, such that $\chi_k = \sum_{\alpha} \psi_{\alpha} U_{\alpha k}$, was introduced, so that $\gamma(x_1' | x_1)$ became diagonal:

$$\gamma(x_1' | x_1) = \sum_k \chi_k^*(x_1') \chi_k(x_1) n_k \quad (1.4)$$

The χ_k 's associated with the exact wave function were called natural spin-orbitals (the others are called approximate natural orbitals; both have symmetry properties if these are included in $\psi^{(13)}$). Unless explicitly stated, we use the words natural spin-orbitals (NSO) for both kinds of functions). When the expansion (1.3) was transformed into the $\{\chi_k\}$ basis, a long forgotten separation theorem due to Cauchy⁽¹⁴⁾ could be applied, and the new expansion coefficients A_K were found to satisfy

$$\sum_{K=1}^r \sum_K^{(k)} |A_K|^2 \geq \sum_{K=1}^r \sum_K^{(k)} |C_K|^2 \quad (1.5)$$

the index k on the left running over the r natural orbitals associated with the highest occupation number n_k (see Eq. (1.4)), and that on the right, running over any r spin-orbitals of $\{\psi_k\}$. This equation is valid for the exact wave function as well as for any approximation to it. Löwdin concludes by pointing out that Eq. (1.5) expresses an optimum convergence property of the natural expansion.

1.2. Practical Importance of NSO Expansions

Here we are going to consider Eq. (1.5) more in detail, so as to specify under which additional conditions it expresses an optimum convergence property. Let us consider the natural expansion

$$\psi = \sum_K \Phi_K A_K$$

and let us subdivide the Slater determinants (SD) into two classes: L and L' . (A justification for this will be found at the end of Section (3.2).) Those in class L are composed of natural orbitals with

occupancy number $n_1 \geq n_2 \geq \dots \geq n_r$ (see Eq. (1.4)); $r \geq N$. Those in class L' may have some SD's (an infinite number perhaps) which include those NSO's showing up in SD's of class L , but in addition, they may have other NSO's χ_i with $n_i \leq n_r$. Equation (1.5) may now be expressed as

$$\sum_{k=1}^r \sum_L \binom{k}{L} |A_L|^2 + \sum_{k=1}^r \sum_{L'} \binom{k}{L'} |A_{L'}|^2 \geq \sum_{k=1}^r \sum_L \binom{k}{L} |C_L|^2 + \sum_{k=1}^r \sum_{L'} \binom{k}{L'} |C_{L'}|^2$$

or

$$N \sum_{\text{all } L} |A_L|^2 + \sum_{k=1}^r \sum_{L'} \binom{k}{L'} |A_{L'}|^2 \geq N \sum_{\text{all } L} |C_L|^2 + \sum_{k=1}^r \sum_{L'} \binom{k}{L'} |C_{L'}|^2 \quad (1.6)$$

If a very careful selection of L -type SD's is made, the second terms on both the left and right hand sides of Eq. (1.6) turn out to be extremely small and

$$\sum_{\text{all } L} |A_L|^2 \geq \sum_{\text{all } L} |C_L|^2 \quad (1.7)$$

expresses the optimum convergence property in a sense which is mathematically understandable. For two electron systems, the second term on the left vanishes and Eq. (1.7) is mandatory under any circumstances. For larger systems, however, the necessary conditions for the fulfillment of Eq. (1.7) are unknown. Not knowing other kinds of linear transformations of the basic spin-orbitals leading to equations similar to (1.4) or (1.6), i.e., leading to equations which under some favorable circumstances may conform to Eq. (1.7), it is worthwhile to examine the consequences of using NSO's in practical applications. It is with this philosophy that we undertake to experiment with NSO expansions.

We believe it is important that the starting wave function be, in a broad sense, a very good approximation to the exact solution. It may be thought that, as the exact solution is approached, the approximate C.I. wave function becomes less dependent on a linear transformation of its spin-orbital basis, and that thus, Eq. (1.7) tends towards an equality. This is incorrect. The answer obviously depends on the relationship between the starting and the final one electron basis, and this cannot be known unless the calculation is performed.

1.3. Application of NSO ideas to Be Ground State

Let us return now to the two electron problem: Löwdin and Shull considered the mean quadratic deviation between the exact solution and a truncated C.I. expansion of a two electron wave function⁽¹⁵⁾, and proved that this quantity is a minimum for the case of the natural expansion, when the latter is truncated to any order r ⁽¹⁶⁾. As these authors pointed out, the preceding situation is equivalent to the diagonalization of a quadratic form. We shall use this fact in the following context: a four electron separated-electron-pair wave function Ω

$$\Omega = \mathcal{A} \{ K(1,2) L(3,4) \}$$

has been shown to be a very good approximation for the ground state of Be⁽¹⁷⁾. We assume then, that an essentially correct $K(1,2)$ function which is presumably localized in the K shell, could be obtained by letting the L shell wave function be $(2s)^2$, i.e. a doubly occupied 2s orbital. We expand $K(1,2)$ as

$$K(1,2) = A \sum_{k \leq 1} \psi_k(x) \psi_1(x) c_{k1} \quad (1.8)$$

in which, of course, ψ_k has opposite spin to ψ_1 and they are always coupled to give a 1S two electron function. The natural K shell spin-orbitals are obtained by diagonalizing the quadratic form in Eq. (1.8), and since they correspond to a two electron function, the truncated natural expansion of $K(1,2)$ will have optimum properties: minimum mean quadratic deviation with respect to the original $K(1,2)$, or, what is equivalent, maximum overlap with it. In this way, a large basis can be effectively reduced, and what is important here is not the obtaining of a basis which represents $K(1,2)$ of Eq. (1.8) in an optimum way, but rather, to get a good basis in which to expand that localized portion of the total wave function, the "physical" K shell, in the general framework of an unrestricted CI calculation.

Since all the basis orbitals are orthogonal, the natural spin-orbitals of $K(1,2)$ are identical with those of $\Omega^{(K)}$

$$\Omega^{(K)} = A \{K(1,2) (2s)^2\} \quad (1.9)$$

except for the addition of two $2s$ spin orbitals with occupancy number equal to one.

We perform the same treatment with a wave function $\Omega^{(L)}$

$$\Omega^{(L)} = A \{(1s)^2 L(3,4)\} \quad (1.10)$$

and, in this fashion, we obtain much information about the best selec-

tion of basis spin-orbitals for our CI calculation. The most important one is to get an answer to the question of how many spin-orbitals of a given symmetry type are energetically effective in describing a given shell. We reserve further comments for Chapter III.

CHAPTER II

ELEMENTS OF A CONFIGURATION INTERACTION TREATMENT

2.1. The Hamiltonian

For small atoms, the relativistic effects are small⁽¹⁸⁾ and it is generally accepted that all aspects of atomic behaviour, with the exception of hyperfine structure, can still be accounted for if one neglects them. In doing so, the Hamiltonian is greatly simplified.

The non-relativistic Hamiltonian H_T , in a frame of reference (x_1, x_2, x_3) centered at the nucleus, is given by

$$H_T = H_{fn} - \frac{m}{2M} \sum_{i,j} \nabla_{x_i} \cdot \nabla_{x_j} \quad (2.1)$$

in atomic units (a.u.; 1 a.u. = twice the non-relativistic energy of the "infinite mass" hydrogen atom ground state). H_{fn} is the conventional "fixed nucleus" non-relativistic Hamiltonian

$$H_{fn} = \sum_i \left(-\frac{1}{2} \Delta_i - \frac{Z}{r_i} \right) + \sum_{i < j} \frac{1}{r_{ij}} \quad (2.2)$$

where m is the rest mass of the electron, M that of the atomic nucleus. A usual approximation⁽¹⁹⁾ to H_T consists in neglecting the off-diagonal terms $-\frac{m}{2M} \sum_{i \neq j} \nabla_{x_i} \cdot \nabla_{x_j}$ in Eq. (2.1). We have

$$H' = H_{fn} - \frac{m}{2M} \sum_i \Delta_i \quad \text{in a.u.} \quad (2.3)$$

If the energy units are now reduced by a multiplicative factor of $(1 - \frac{m}{2M})$, we obtain the modified atomic units (m.a.u.) for the nucleus in consideration⁽²⁰⁾. The new Hamiltonian H is given by

$$H = \sum_i \left(-\frac{1}{2} \Delta_i - \frac{Z}{r_i} \right) + \sum_{i < j} \frac{1}{r_{ij}} \quad (2.4)$$

and we have

$$H' \text{ (a.u.)} = H \text{ (m.a.u.)}$$

We shall use H throughout this calculation.

2.2. Basic Slater Determinants and Spin-orbitals

We consider only normalized Slater determinants D ⁽²¹⁾

$$D = (N!)^{\frac{1}{2}} \mathcal{A} \{ \psi_1(x_1) \psi_2(x_2) \dots \psi_N(x_N) \}$$

$$\mathcal{A} = \frac{1}{N!} \sum_P (-1)^P P \quad ; \mathcal{A}^2 = \mathcal{A} \quad ; \mathcal{A} = \mathcal{A}^\dagger$$

made up of orthonormal, symmetry adapted spin-orbitals $\psi_\mu(x)$ in which $\mu = \mu(i, \ell, m_\ell, m_s)$:

$$\psi_{i \ell m_\ell m_s} = R_{i \ell}(r) Y_{\ell m_\ell}(\vartheta, \phi) \xi_{m_s}(\sigma_s) \quad (2.5)$$

The set $\{Y_{\ell m_\ell}\}$ consists of normalized spherical harmonics in the Dirac phase convention⁽¹⁹⁾, and $\{\xi_{m_s}\}$ are the usual spin functions

α, β with eigenvalues $m_\ell = \pm \frac{1}{2}$. The set of functions $\{R_{i\ell}\}$ is expanded in terms of normalized Slater type orbitals (STO's) $S_{j\ell}$ ⁽²²⁾ with $j = 1, 2, \dots, J(\ell)$:

$$R_{i\ell} = \sum_j^{J(\ell)} S_{j\ell} a_{j\ell i} \quad (2.6)$$

$$S_{j\ell} = N_{j\ell} r^{(n_j + \ell)} \exp(-Z_{j\ell} r) \quad (2.7)$$

$$N_{j\ell} = \left[(2Z_{j\ell})^{(2\ell + 2n_j + 3)} / (2\ell + 2n_j + 2)! \right]^{\frac{1}{2}}$$

and we have further the normalization condition

$$\int R_{i\ell}(r) R_{i'\ell}(r) r^2 dr = \delta_{ii'}$$

The n_j 's are integers and $n_j \geq 0$; the values $n_j = 0$, and $n_j = 1$ are always included. Higher terms are introduced when the number of orbital exponents $Z_{j\ell}$ for each value of ℓ is less than three. There is no permanent reason for this: it arises from previous experience of other authors⁽²³⁾ as well as our own. Anyway, there is not much point in simplifying further the expansion (2.6) at this stage; we shall come back to this point later, in Chapter III. The powers of r in Eq. (2.7) are $(n_j + \ell)$, the ℓ being present in order to make $\{\psi_\mu\}$ be in the domain of the Hamiltonian: specifically, so that some integrals involving the operator $1/r_{12}$ do not blow up. The starting orbital exponents $Z_{j\ell}$ are selected by trial and error. In general, when optimization (with respect to total energy) is desired, a brute force method is employed. The previous experience of other workers indicates that a careful optimization does not pay⁽²³⁾, and that

once some reasonable Z_{jl} are obtained, it is much better to introduce additional configurations. However, this is true up to a certain stage, after which the CI expansion appears to converge very slowly. Then, it is desirable to think about an orbital exponent optimization, which does not need to be done by brute force alone, since by now, much more is known about the regions where the electronic density probability is localized. Further comments shall be made in Chapter IV.

In order to get started on our calculation, and because an initial optimization of orbital exponents was impractical with an IBM 709, we were compelled to assume that orbital exponents which give a good HF ground state could also be used to form an STO basis which is essentially correct. For orbital exponents corresponding to orbitals with an l value not represented in the ground configuration, an "excited configuration" was considered, in which some ground state orbitals have been replaced by those in question, and the energy was optimized while keeping the remaining ground state orbitals fixed: this was done by Watson in his treatment of Be⁽²³⁾. Summarizing, two main elements are employed in the preliminary search for the one electron functions: the HF orbitals, and an associated STO basis defined in terms of the orbital exponents and of the n_j power exponents. The problem consists then, in obtaining an orthogonal basis of a dimension smaller than that of the STO basis and which is convenient for a CI treatment. Watson⁽²³⁾ used a method which employed successive Schmidt orthogonalizations of the STO's, combined with second order perturbation theory estimates of the CI effects introduced by some

"selected configurations." For more details, the reader is referred to Watson's paper. It is interesting to note that additional functions of a given symmetry type were introduced in his calculation until further additions contributed to the energy with less than 0.00005 a.u. At first sight, the method may seem quite laborious; however, the whole process can be carried out automatically on an electronic computer, in a very simple way.

An apparent shortcoming arises in the choice of the "selected configurations" to be used in each case. It presupposes a knowledge of which configurations are dominant, which may or may not be correct. As a result, the "selected configurations" do become artificially dominant. By including a reasonable variety of "selected configurations" this difficulty is overcome. Second order energy estimates are highly desirable, as they are a cheap alternative to a rigorous total energy criterion, which, after all, does not necessarily lead to a better choice of one electron functions.

However, from the results of Weiss' subsequent work on Be⁽²⁴⁾ and from the recent investigation of Miller and Ruedenberg⁽²⁵⁾, we developed the conviction that Watson's one electron functions could be significantly improved simply by modifying the expansion coefficients $\{a_{jli}\}$ while leaving the STO basis intact. It seemed possible that some important configurations be missing in Watson's wave function. Obviously, we needed to find a better method for the search of spin-orbitals.

Our conviction had less to do with a scientific analysis

than with a genuine interest in the general applicability of the C.I. method. Weiss' basis was not orthogonal and he reached a limit where the mathematical stability of his secular equation made it impossible to add generously some much needed configurations. The transformation to an orthogonal spin-orbital basis would have increased the number of configurations in a manner probably unnecessary and impractical⁽²⁶⁾. Thus, as Weiss stated in his paper, his results could not be improved significantly along the same line of work, and he drew a pessimistic conclusion with which we could not agree. On the other hand, Miller and Ruedenberg's approach seems to be general in theory as well as in practice, and many stimulating results have been obtained and are to be expected in the future. Their wave function is just an intelligently constrained C.I. wave function. Since there is always time to decide at which stage and how to impose constraints on a C.I. wave function, we choose to follow the lines of the conventional C.I. method.

2.3. Basic Functions

A pure basis is one whose elements are eigenfunctions to some set of quantum mechanical operators. When these operators commute with some Hamiltonian, the introduction of symmetric projection operators brings about, not only a method for the obtaining of the pure basis⁽²⁷⁾, but also some important simplifications in the secular equation and in the matrix elements corresponding to that Hamiltonian⁽²⁷⁾; this is the reason for using a pure basis (the pure basis alone simplifies the secular equation; when it is obtained by means

of symmetric projection operators, the matrix elements are also simplified).

In the atomic case, the electrostatic Hamiltonian H commutes with L^2 , L_z , S^2 , S_z (squares and z -components of the total orbital and spin angular momentum) and with \mathcal{P} , the parity operator. Thus, we use a basis of eigenfunctions to $\{L^2, L_z, S^2, S_z, \mathcal{P}\}$. When looking for the variational solutions to H corresponding to a given set of eigenvalues to $\{L^2, L_z, S^2, S_z, \mathcal{P}\}$, we need to concentrate only on the subsecular equation (of infinite order, however) associated with the above mentioned eigenvalues.

The projection operators \mathcal{O} considered here, were introduced by Löwdin⁽²⁸⁾; they are idempotent, hermitian and symmetric (so that they commute with H):

$$\mathcal{O}^2 = \mathcal{O} = \mathcal{O}^\dagger \quad ; \quad \mathcal{O}(x_1, x_2, \dots, x_N) = \mathcal{P} \mathcal{O}(x_1, x_2, \dots, x_N)$$

and may be expressed as

$$\mathcal{O}_k^\Lambda = \prod_{\ell \neq k} \frac{\Lambda - \lambda_\ell}{\lambda_k - \lambda_\ell} \quad (2.8)$$

where Λ fulfills

$$\Lambda \phi_\ell = \lambda_\ell \phi_\ell$$

and

$$\mathcal{O}_k^\Lambda \phi = \mathcal{O}_k^\Lambda \left(\sum_\ell \phi_\ell c_\ell \right) = \phi_k c_k \quad (2.9)$$

that is, \mathcal{O}_k^Λ selects the component of ϕ which is an eigenfunction to Λ with eigenvalue λ_k . We will be concerned only with $\Lambda = L^2$ and

$\Lambda = S^2$, since when symmetry adapted spin-orbitals are used, the determinantal functions are already eigenfunctions to L_z , S_z and parity. The projection operator employed will be the product of $O_L^{L^2}$ times $O_S^{S^2}$

$$O_{L,S}^{L^2, S^2} = O_L^{L^2} \cdot O_S^{S^2}$$

The functions ϕ upon which the projection operator acts, are a set of orthonormal Slater determinants $D_{K\alpha}$; K denotes the particular configuration and α classifies the possible determinants in configuration K (a configuration is defined by the ordered set of all (i, ℓ) numbers associated with the spin-orbitals $\psi_{i\ell m_\ell m_s}$ which form a given determinantal function).

Some configurations allow for only one linearly independent projected function corresponding to a given set of L, L_z, S, S_z values (each configuration has already a given parity equal to $(-1)^{\sum \ell_i}$). Such pure functions are called non-degenerate. When more than one linearly independent function can be obtained, these functions are called degenerate.

The orthonormal set of pure functions $\Phi_K^{(p)}$ can be expressed as

$$\Phi_K^{(p)} = O_{L,S}^{L^2, S^2} \left[\sum_{\alpha=1}^p D_{K\alpha} b_{K\alpha}^{(p)} \right] = \sum_{\alpha=1}^{n_K} D_{K\alpha} c_{K\alpha}^{(p)} \quad (2.10)$$

In addition, the following relations are fulfilled

$$\left[O_{L,S}^{L^2, S^2} \right]^2 = O_{L,S}^{L^2, S^2}$$

$$\langle \Phi_K^{(p)} | \Phi_L^{(q)} \rangle = \delta_{KL} \delta_{pq}$$

The superscripts p and q denote the p^{th} and q^{th} elements of the orthonormal pure functions associated with the configuration K and L and with the degeneracies g_K and g_L respectively. The purpose of writing the above equations is to obtain neat expressions for the matrix elements of H . We have

$$\begin{aligned} H_{K,L}^{(p,q)} &= \langle \Phi_K^{(p)} | H | \Phi_L^{(q)} \rangle \\ &= \sum_{\alpha=1}^p \sum_{\beta=1}^{n_K} b_{K\alpha}^{(p)} c_{L\beta}^{(q)} \langle D_{K\alpha} | H | D_{L\beta} \rangle \end{aligned} \quad (2.11)$$

where we have made use of the relations

$$\mathcal{O}^2 = \mathcal{O} = \mathcal{O}^\dagger \quad \text{and} \quad \mathcal{O}_H = H \mathcal{O}.$$

Equation (2.11) differs from the one given by Löwdin⁽²⁷⁾, in that the summation starts with $\beta=1$ instead of $\beta=q$, the definitions of the b 's and c 's being somewhat different. Our equation contemplates a simpler computer program. When working by hand, or in the case of large degeneracies, the matrix elements are more readily computed by means of the Löwdin's formula.

In addition, when gathering data to be fed into the computer, it is worthwhile to present them as simply as possible, to avoid mistakes which otherwise may remain undetected. Thus, our starting set of pure functions shall be, instead:

$$\varphi_K^{(p)} = \sum_{\alpha=1}^{n_K} D_{K\alpha} d_{K\alpha}^{(p)} = M_K^{(p)} [\mathcal{O}_{D_{Kp}}] \quad (2.12)$$

To obtain the $b_{K\gamma}^{(m)}$ coefficients, equation (2.13m) is rewritten as

$$\begin{aligned}\Phi_K^{(m)} &= N_K^{(m)} \left[-\sum_{p=1}^{m-1} \left(\sum_{\alpha=1}^p b_{K\alpha}^{(p)} d_{K\alpha}^{(m)} \right) \left\{ \mathcal{O} \left(\sum_{\gamma=1}^p D_{K\gamma} b_{K\gamma}^{(p)} \right) \right\} + M_K^{(m)} \mathcal{O}_{D_{Km}} \right] \\ &= N_K^{(m)} \left[\sum_{\gamma=1}^{m-1} D_{K\gamma} \left\{ -\sum_{p=\gamma}^{m-1} \left(\sum_{\alpha=1}^p b_{K\alpha}^{(p)} d_{K\alpha}^{(m)} \right) b_{K\gamma}^{(p)} \right\} + M_K^{(m)} D_{Km} \right] \quad (2.16)\end{aligned}$$

Thus, we have the unnormalized coefficients $\bar{b}_{K\gamma}^{(m)}$

$$\bar{b}_{K\gamma}^{(m)} = -\sum_{p=\gamma}^{m-1} \left(\sum_{\alpha=1}^p b_{K\alpha}^{(p)} d_{K\alpha}^{(m)} \right) b_{K\gamma}^{(p)} \quad \text{for } \gamma < m$$

$$\bar{b}_{Km}^{(m)} = M_K^{(m)}$$

and the normalized coefficients $b_{K\gamma}^{(m)}$ are then

$$b_{K\gamma}^{(m)} = \bar{b}_{K\gamma}^{(m)} \left(\sum_{\alpha=1}^{n_K} \{ \bar{c}_{K\alpha}^{(m)} \}^2 \right)^{-\frac{1}{2}} \quad (2.17)$$

The constant $M_K^{(m)}$ is easily obtained from Eq. (2.12) as

$$M_K^{(m)} = \sum_{\alpha=1}^{n_K} \{ d_{K\alpha}^{(m)} \}^2 / d_{Km}^{(m)} \quad (2.18)$$

2.4. Basic Configurations

In the previous section, the basic many electron functions were introduced in a most general way. It is our purpose now to deal with the question of degeneracies and of how to obtain, in practice, the coefficients $\{ d_{K\alpha}^{(p)} \}$.

Today, computer programs are available to carry out L^2 and S^2 projections of Slater determinants made up of symmetry adapted spin-orbitals⁽²⁹⁾ (the orbital quantum number ℓ must not exceed the value $\ell = 4$, in case a machine of reduced core storage, like the IBM 709, is being used; some special cases involving higher ℓ values are also feasible in that machine). Furthermore, the degeneracies of the terms that appear in each case have been well studied⁽³⁰⁾ and they can be evaluated by means of existing computer programs⁽²⁹⁾. In spite of this, we thought that our application to even $1S$ states of Be was so simple that it would be far more amusing to do this by hand, instead of spending our time trying to make operational, computer programs which had been written by others. It is instructive to do this once in a life time; next time, we hope to use the electronic computer.

The determination of degeneracies is very simple. First, all equivalent spin-orbitals (those with the same (i, ℓ) numbers) are grouped, and the possible terms of each group are found according to the Pauli principle: no more than one electron for each spin-orbital. Then, all possible terms arising from all groups of equivalent electrons are coupled together, and without restrictions, according to the rules of addition of angular momenta. For instance, the configuration $(s)^2(p)^2$ has two groups of equivalent electrons. The arrangement $(s)^2$ can give only a $1S$ term, while $(p)^2$ gives three terms: $1D$, $3P$ and $1S$. Of the latter, only the $1S$ can be coupled with the other $1S$ to give a four electron $1S$. Thus, the degeneracy is equal to one.

The configuration $ss'pp'$, instead, is doubly degenerate: s and s' may be combined to give two terms: 1S and 3S ; while from p and p' one may obtain: 1S , 3S , 1P , 3P , 1D and 3D . The two possible four electron 1S terms arise from combining $(ss')^1S$ with $(pp')^1S$ and $(ss')^3S$ with $(pp')^3S$.

As for the angular momentum and spin projection, Löwdin expands L^2 in terms of $L_+ = L_x + iL_y$ and $L_- = L_x - iL_y$ (step-up and step-down operators) and similarly for S^2 :

$$\begin{aligned} L^2 &= L_- L_+ + L_z^2 - L_z \\ S^2 &= S_- S_+ + S_z^2 - S_z \end{aligned} \quad (2.19)$$

By substituting from Eq. (2.19) into Eq. (2.8) he obtains, in general (31)

$$\mathcal{O}_{M, M_z}^{M^2} = (2M+1) \frac{(M+M_z)!}{(M-M_z)!} \sum_{\nu=0}^{M_{\max}-M} (-1)^\nu \frac{\hat{M}_-^{(M-M_z+\nu)} \hat{M}_+^{(M-M_z+\nu)}}{\nu! (2M+\nu+1)!} \quad (2.20)$$

where M stands for either L or S and the caret distinguishes between operator and quantum number; M_{\max} depends on the particular configuration and is obtained according to the rules of addition of the general angular momenta. For the particular case of the 1S terms, we have

$$\mathcal{O}_{00}^{M^2} = \sum_{\nu=0}^{M_{\max}} (-1)^\nu \frac{\hat{M}_-^\nu \hat{M}_+^\nu}{\nu! (\nu+1)!} \quad (2.21)$$

In Table 1, we give the non-degenerate configurations employed in this work, together with the projected functions and the d coefficient.

cients. Table 2 shows the doubly degenerate configurations and Table 3, the triply degenerate ones. In the columns labeled $d^{(1)}$, $d^{(2)}$, $d^{(3)}$ corresponding to different functions of the degenerate set, we also have indicated which Slater determinant was projected in each case. We always performed the L^2 projection first, and then, the spin projection. Those configurations having only s-type orbitals need a spin projection only, and they were projected exactly according to Eq. (2.9), i.e. $M_K^{(p)} = 1$ (see Eq. (2.12)). The latter results were in turn applied directly to the L^2 projections of the more general configurations. In the normalized Slater determinant $(i \begin{smallmatrix} a & j & b \\ w & x & y \end{smallmatrix} | k \begin{smallmatrix} c & 1 & d \\ y & z & \end{smallmatrix})$, the letters i, j, k, l stand for the l quantum number, the superscripts a, b, c, d, for m_l ; the subscripts w, x, y, z stand for the quantum number i: in these tables they are included only to distinguish between groups of equivalent electrons and they are arbitrary otherwise; finally, the orbitals to the left of the bar are associated with α spin, those to the right, with β spin.

TABLE 1

NON DEGENERATE CONFIGURATIONS

Configuration	Slater determinants	d coefficients
$(s_w)^2(s_x)^2$	$(s_w s_x s_w s_x)$	1
$(s_w)^2 s_x s_y$	$(s_w s_x s_w s_y)$	$\frac{1}{2}$
	$(s_w s_y s_w s_x)$	$\frac{1}{2}$
$(s)^2(p)^2$	$(s p^0 s p^0)$	1
	$(s p^1 s p^1)$	-1
	$(s p^1 s p^1)$	-1
$s_w s_x (p)^2$	$(s_w p^0 s_x p^0)$	1
	$(s_x p^0 s_w p^0)$	1
	$(s_w p^1 s_x p^1)$	-1
	$(s_x p^1 s_w p^1)$	-1
	$(s_w p^1 s_x p^1)$	-1
	$(s_x p^1 s_w p^1)$	-1
$(s)^2 p_w p_x$	$(s p_w^0 s p_x^0)$	1
	$(s p_x^0 s p_w^0)$	1
	$(s p_w^1 s p_x^1)$	-1
	$(s p_x^1 s p_w^1)$	-1
	$(s p_w^1 s p_x^1)$	-1

TABLE 1 continued

Configuration	Slater determinants	d coefficients
	$(s \ p_x^1 s \ p_w^1)$	-1
$(p)^4$	$(p^1 p^0 p^0 p^1)$	1
	$(p^0 p^1 p^1 p^0)$	1
	$(p^1 p^1 p^1 p^1)$	-1
$(p_w)^3 p_x$	$(p_w^1 p_w^0 p_w^0 p_x^1)$	1
	$(p_w^0 p_x^1 p_w^1 p_w^0)$	1
	$(p_w^1 p_w^1 p_w^1 p_x^1)$	-1
	$(p_w^1 p_x^1 p_w^1 p_w^1)$	-1
	$(p_w^1 p_w^0 p_w^1 p_w^0)$	-1
	$(p_w^1 p_x^0 p_w^1 p_w^0)$	-1
	$(p_w^0 p_w^1 p_w^1 p_x^0)$	1
	$(p_w^1 p_x^0 p_w^0 p_w^1)$	1
	$(p_w^0 p_w^1 p_w^0 p_x^1)$	-1
	$(p_w^0 p_x^1 p_w^0 p_w^1)$	-1
	$(p_w^1 p_w^1 p_w^1 p_x^1)$	1
	$(p_w^1 p_x^1 p_w^1 p_w^1)$	1
$(s)^2 (d)^2$	$(s \ d^0 s \ d^0)$	1
	$(s \ d^1 s \ d^1)$	-1
	$(s \ d^1 s \ d^1)$	-1

TABLE 1 continued

Configuration	Slater determinants	d coefficients
	$(s d^2 s d^2)$	1
	$(s d^2 s d^2)$	1
$(s)^2 d_w d_x$	$(s d_w^0 s d_x^0)$	1
	$(s d_x^0 s d_w^0)$	1
	$(s d_w^1 s d_x^1)$	-1
	$(s d_x^1 s d_w^1)$	-1
	$(s d_w^1 s d_x^1)$	-1
	$(s d_x^1 s d_w^1)$	-1
	$(s d_w^2 s d_x^2)$	1
	$(s d_x^2 s d_w^2)$	1
	$(s d_w^2 s d_x^2)$	1
	$(s d_x^2 s d_w^2)$	1
$s(p)^2 d$	$(s p^0 p^0 d^0)$	4
	$(p^0 d^0 s p^0)$	4
	$(s p^1 p^1 d^2)$	$\sqrt{24}$
	$(p^1 d^2 s p^1)$	$\sqrt{24}$
	$(s p^1 p^1 d^2)$	$\sqrt{24}$
	$(p^1 d^2 s p^1)$	$\sqrt{24}$
	$(s p^0 p^1 d^1)$	$-\sqrt{12}$
	$(p^1 d^1 s p^0)$	$-\sqrt{12}$

TABLE 1 continued

Configuration	Slater determinants	d coefficients
	$(s \ p^1 \ p^0 \tilde{d}^1)$	$-\sqrt{12}$
	$(p^0 \tilde{d}^1 \ s \ p^1)$	$-\sqrt{12}$
	$(s \ \tilde{p}^1 \ p^0 \tilde{d}^1)$	$-\sqrt{12}$
	$(p^0 \tilde{d}^1 \ s \ \tilde{p}^1)$	$-\sqrt{12}$
	$(s \ p^0 \ \tilde{p}^1 \tilde{d}^1)$	$-\sqrt{12}$
	$(\tilde{p}^1 \tilde{d}^1 \ s \ p^0)$	$-\sqrt{12}$
	$(s \ \tilde{p}^1 \ p^1 \tilde{d}^0)$	2
	$(p^1 \tilde{d}^0 \ s \ \tilde{p}^1)$	2
	$(s \ p^1 \ \tilde{p}^1 \tilde{d}^0)$	2
	$(\tilde{p}^1 \tilde{d}^0 \ s \ p^1)$	2
$s \ (d_w)^2 d_x$	$(s \ d_w^0 \ d_w^0 \tilde{d}_x^0)$	2
	$(d_w^0 \tilde{d}_x^0 \ s \ d_w^0)$	2
	$(s \ \tilde{d}_w^1 \ d_w^1 \tilde{d}_x^0)$	-1
	$(d_w^1 \tilde{d}_x^0 \ s \ \tilde{d}_w^1)$	-1
	$(s \ d_w^1 \ \tilde{d}_w^1 \tilde{d}_x^0)$	-1
	$(\tilde{d}_w^1 \tilde{d}_x^0 \ s \ d_w^1)$	-1
	$(s \ d_w^0 \ d_w^1 \tilde{d}_x^1)$	-1
	$(d_w^1 \tilde{d}_x^1 \ s \ d_w^0)$	-1
	$(s \ \tilde{d}_w^1 \ d_w^0 \tilde{d}_x^1)$	-1
	$(d_w^0 \tilde{d}_x^1 \ s \ \tilde{d}_w^1)$	-1
	$(s \ \tilde{d}_w^1 \ d_w^0 \tilde{d}_x^1)$	-1
	$(d_w^0 \tilde{d}_x^1 \ s \ \tilde{d}_w^1)$	-1

TABLE 1 continued

Configuration	Slater determinants	d coefficients
	$(d_w^0 d_x^1 s \bar{d}_w^1)$	-1
	$(s d_w^0 d_w^1 d_x^1)$	-1
	$(\bar{d}_w^1 d_x^1 s d_w^0)$	-1
	$(s \bar{d}_w^2 d_w^1 d_x^1)$	$\sqrt{6}$
	$(d_w^1 d_x^1 s \bar{d}_w^2)$	$\sqrt{6}$
	$(s d_w^1 \bar{d}_w^2 d_x^1)$	$\sqrt{6}$
	$(\bar{d}_w^2 d_x^1 s d_w^1)$	$\sqrt{6}$
	$(s \bar{d}_w^1 d_w^2 d_x^1)$	$\sqrt{6}$
	$(d_w^2 d_x^1 s \bar{d}_w^1)$	$\sqrt{6}$
	$(s d_w^2 \bar{d}_w^1 d_x^1)$	$\sqrt{6}$
	$(\bar{d}_w^1 d_x^1 s d_w^2)$	$\sqrt{6}$
	$(s d_w^1 d_w^1 d_x^2)$	$\sqrt{6}$
	$(d_w^1 d_x^2 s d_w^1)$	$\sqrt{6}$
	$(s \bar{d}_w^1 d_w^1 d_x^2)$	$\sqrt{6}$
	$(\bar{d}_w^1 d_x^2 s \bar{d}_w^1)$	$\sqrt{6}$
	$(s \bar{d}_w^2 d_w^2 d_x^0)$	-2
	$(d_w^2 d_x^0 s \bar{d}_w^2)$	-2
	$(s d_w^2 \bar{d}_w^2 d_x^0)$	-2
	$(\bar{d}_w^2 d_x^0 s d_w^2)$	-2
	$(s d_w^0 d_w^2 d_x^2)$	-2
	$(d_w^2 d_x^2 s d_w^0)$	-2

TABLE 1 continued

Configuration	Slater determinants	d coefficients
	$(s d_w^2 d_w^0 \tilde{d}_x^2)$	-2
	$(d_w^0 \tilde{d}_x^2 s d_w^2)$	-2
	$(s d_w^2 d_w^0 \tilde{d}_x^2)$	-2
	$(d_w^0 \tilde{d}_x^2 s d_w^2)$	-2
	$(s d_w^0 \tilde{d}_w^2 \tilde{d}_x^2)$	-2
	$(\tilde{d}_w^2 \tilde{d}_x^2 s d_w^0)$	-2

TABLE 2

DOUBLY DEGENERATE CONFIGURATIONS

Configuration	Slater determinants	$d^{(1)}$	$d^{(2)}$
		$(s_w s_y s_x s_z)$	$(s_w s_x s_y s_z)$
$s_w s_x s_y s_z$	$(s_w s_y s_x s_z)$	1/3	1/6
	$(s_w s_x s_y s_z)$	1/6	1/3
	$(s_x s_z s_w s_y)$	1/3	1/6
	$(s_y s_z s_w s_x)$	1/6	1/3
	$(s_w s_z s_x s_y)$	1/6	-1/6
	$(s_x s_y s_w s_z)$	1/6	-1/6
$s_w s_x s_y s_z$		$(s_w p_y^0 s_x p_z^0)$	$(s_w p_z^0 s_x p_y^0)$
	$(s_w p_y^0 s_x p_z^0)$	1	1/2
	$(s_w p_z^0 s_x p_y^0)$	1/2	1
	$(s_w p_y^1 s_x p_z^1)$	-1	-1/2
	$(s_x p_z^1 s_w p_y^1)$	-1	-1/2
	$(s_w p_y^1 s_x p_z^1)$	-1	-1/2
	$(s_x p_z^1 s_w p_y^1)$	-1	-1/2
	$(s_w s_x p_y^0 p_z^0)$	1/2	-1/2
	$(p_y^0 p_z^0 s_w s_x)$	1/2	-1/2
	$(s_w s_x p_y^1 p_z^1)$	-1/2	1/2
	$(p_y^1 p_z^1 s_w s_x)$	-1/2	1/2
	$(s_w s_x p_y^1 p_z^1)$	-1/2	1/2
	$(p_y^1 p_z^1 s_w s_x)$	-1/2	1/2
	$(p_y^1 p_z^1 s_w s_x)$	-1/2	1/2

TABLE 2 continued

Configuration	Slater determinants	$d^{(1)}$	$d^{(2)}$
	$(s_x^0 p_z^0 s_w^0 p_y^0)$	1	1/2
	$(s_x^0 p_y^0 s_w^0 p_z^0)$	1/2	1
	$(s_w^1 p_z^{-1} s_x^1 p_y^{-1})$	-1/2	-1
	$(s_x^1 p_y^{-1} s_w^1 p_z^1)$	-1/2	-1
	$(s_w^1 p_z^{-1} s_x^1 p_y^1)$	-1/2	-1
	$(s_x^1 p_y^1 s_w^1 p_z^{-1})$	-1/2	-1

TABLE 3

TRIPLY DEGENERATE CONFIGURATIONS

Configuration	Slater determinants	d(1)	d(2)	d(3)
		$(p_w^1 p_x^0 p_w^0 p_y^{-1})$	$(p_w^0 p_x^1 p_w^0 p_y^{-1})$	$(p_w^1 p_w^0 p_x^0 p_y^{-1})$
$(p_w)^2 p_x p_y$	$(p_w^1 p_x^0 p_w^0 p_y^{-1})$	7	-3	1
	$(p_w^0 p_x^1 p_w^0 p_y^{-1})$	-3	12	0
	$(p_w^1 p_w^0 p_x^0 p_y^{-1})$	5	0	2
	$(p_w^0 p_y^{-1} p_w^1 p_x^0)$	7	-3	1
	$(p_w^0 p_x^1 p_w^1 p_y^0)$	7	-3	1
	$(p_w^{-1} p_y^0 p_w^0 p_x^1)$	7	-3	1
	$(p_w^0 p_x^1 p_w^1 p_y^0)$	7	-3	1
	$(p_w^1 p_y^0 p_x^0 p_y^{-1})$	7	-3	1
	$(p_x^0 p_y^{-1} p_w^1 p_x^0)$	7	-3	1
	$(p_w^1 p_x^0 p_w^0 p_y^{-1})$	7	-3	1
	$(p_x^0 p_y^{-1} p_w^1 p_x^0)$	5	0	2
	$(p_w^0 p_w^0 p_x^0 p_y^{-1})$	5	0	2
	$(p_x^1 p_y^0 p_w^0 p_w^0)$	5	0	2
	$(p_w^1 p_w^0 p_x^0 p_y^{-1})$	5	0	2
	$(p_w^1 p_w^0 p_x^0 p_y^{-1})$	-5	0	-2
	$(p_x^1 p_y^0 p_w^1 p_w^0)$	-5	0	-2
	$(p_w^0 p_y^{-1} p_x^0 p_y^{-1})$	-5	0	-2
	$(p_x^0 p_y^{-1} p_w^0 p_w^0)$	-5	0	-2
	$(p_w^1 p_y^0 p_w^0 p_x^0)$	2	-3	-1
	$(p_w^0 p_x^1 p_w^1 p_y^0)$	2	-3	-1

TABLE 3 continued

Configuration	Slater determinants	$d^{(1)}$	$d^{(2)}$	$d^{(3)}$
	$(\bar{p}_w^1 p_x^1 \bar{p}_w^1 p_y^1)$	1	-9	1
	$(\bar{p}_w^1 p_y^1 \bar{p}_w^1 p_x^1)$	1	-9	1
	$(\bar{p}_w^1 p_x^1 \bar{p}_w^1 p_y^1)$	1	-9	1
	$(\bar{p}_w^1 p_y^1 \bar{p}_w^1 p_x^1)$	-9	6	0
	$(\bar{p}_w^1 p_x^1 \bar{p}_w^1 p_y^1)$	-9	6	0
	$(\bar{p}_w^1 p_x^1 \bar{p}_w^1 p_y^1)$	-9	6	0
	$(\bar{p}_w^1 p_y^1 \bar{p}_w^1 p_x^1)$	-9	6	0
	$(\bar{p}_w^1 p_y^1 \bar{p}_w^1 p_x^1)$	-9	6	0
	$(p_w^0 p_x^0 p_w^0 p_y^0)$	-6	-6	0
	$(p_w^0 p_y^0 p_w^0 p_x^0)$	-6	-6	0
		$(\bar{p}_w^1 p_x^0 p_w^0 p_x^1)$	$(p_w^0 p_x^1 p_w^0 p_x^1)$	$(\bar{p}_w^1 p_x^0 p_w^0 p_x^1)$
$(p_w)^2 (p_x)^2$	$(\bar{p}_w^1 p_x^0 p_w^0 p_x^1)$	7	-3	1
	$(p_w^0 p_x^1 p_w^0 p_x^1)$	-3	12	0
	$(\bar{p}_w^1 p_w^0 p_x^0 p_x^1)$	5	0	2
	$(p_w^0 p_x^1 \bar{p}_w^1 p_x^0)$	7	-3	1
	$(p_w^0 p_x^1 \bar{p}_w^1 p_x^0)$	7	-3	1
	$(\bar{p}_w^1 p_x^0 p_w^0 p_x^1)$	7	-3	1
	$(p_x^0 p_x^1 \bar{p}_w^1 p_w^0)$	5	0	2
	$(p_w^0 p_x^1 \bar{p}_w^1 p_x^0)$	5	0	2
	$(p_x^1 p_x^0 p_w^0 p_w^0)$	5	0	2
	$(\bar{p}_w^1 p_x^1 p_w^0 p_x^0)$	2	-3	-1

TABLE 3 continued

Configuration	Slater determinants	$d^{(1)}$	$d^{(2)}$	$d^{(3)}$
	$(p_w^0 p_x^0 p_w^1 p_x^{-1})$	2	-3	-1
	$(p_w^0 p_x^0 p_w^1 p_x^1)$	2	-3	-1
	$(p_w^{-1} p_x^1 p_w^0 p_x^0)$	2	-3	-1
	$(p_w^0 p_x^{-1} p_w^0 p_x^1)$	-3	12	0
	$(p_w^1 p_x^0 p_w^{-1} p_x^0)$	-3	12	0
	$(p_w^{-1} p_x^0 p_w^1 p_x^0)$	-3	12	0
	$(p_w^1 p_x^1 p_w^{-1} p_x^{-1})$	-4	-9	-1
	$(p_w^{-1} p_x^{-1} p_w^1 p_x^1)$	-4	-9	-1
	$(p_w^1 p_x^{-1} p_w^1 p_x^{-1})$	-5	0	-2
	$(p_x^1 p_x^{-1} p_w^1 p_w^{-1})$	-5	0	-2
	$(p_w^1 p_x^{-1} p_w^{-1} p_x^1)$	1	-9	1
	$(p_w^{-1} p_x^1 p_w^1 p_x^{-1})$	1	-9	1
	$(p_w^1 p_x^{-1} p_w^1 p_x^{-1})$	-9	6	0
	$(p_w^{-1} p_x^1 p_w^1 p_x^{-1})$	-9	6	0
	$(p_w^0 p_x^0 p_w^0 p_x^0)$	-6	-6	0

CHAPTER III

CALCULATION

3.1. The STO Basis

We employed the STO basis previously used by Watson⁽²³⁾, to expand s-, p- and d-type orbitals. In his calculation, Watson considered f- and g-type orbitals also; these were not considered here.

Watson's choice of orbital exponents was based on previous experience from his own calculations on the He ground state⁽³²⁾. We checked his HF orbitals by running Roothaan's atomic SCF program⁽³³⁾ on the IBM 709 computer, while keeping Watson's STO's fixed; we found them correct to all ciphers in the energy and at least to five figures in the orbitals. The STO basis is given in Table 4, for completeness. As a result of limiting ourselves to only two orbital exponents for each type of orbital symmetry, it was possible to include several powers of r without much programming effort. Watson's compromise of two orbital exponents and n_j values up to $n_j=4$ for s-type orbitals, is very similar to the option chosen by Weiss, who combined only one n_j value, either $n_j=0$ or $n_j=1$, with each of four orbital exponents.

TABLE 4

THE STO BASIS

	j=1	2	3	4	5	6	7	8	9
$n_j=0$	0	1	1	2	2	3	3	4	
z_{j1}	6.0	1.0	6.0	1.0	6.0	1.0	6.0	1.0	6.0
z_{j2}	9.0	1.5	9.0	1.5	9.0	1.5	9.0		
z_{j3}	12.0	2.0	12.0	2.0	12.0				

3.2. The Search for s and p Orbitals

According to the scheme outlined in Section 1.3, we performed CI calculations based on Eqs. (1.9) and (1.10) and with s- and p-type orbitals only. Two different sets of spin-orbitals were employed as a basis: set A was made up of the NSO's of Watson's wave function (23) as calculated by Barnett⁽²⁶⁾; set B consisted of a trial basis: the orbitals s_1 , s_2 and p_1 were taken to be, in order, the 1s, 2s and p_1 of Watson. Additional orbitals, up to s_7 and p_5 , are constructed by successive Schmidt orthogonalization of the STO basis according to the order $j=2,3,5,6,7$ for s-type orbitals and $j=1,3,4,5,6$ for p-type orbitals..

The results are displayed in Table 5. The energy differences between CI results obtained with the two basic sets are not considered to be significant. In Table 12, the occupation number spectra of some of these wave functions are shown. The resemblances between the occupation numbers of the K and L shell CI NSO's of set B with some of those from the Weiss wave function, are striking. The K and L shell NSO's are very complementary, in the sense that, when one of them, say, from the K shell wave function, has a relatively high occupation number, the corresponding NSO for the L shell has a very small one, and vice versa (the NSO's from both K and L shell CI were classified by comparing their plottings with those from the KL shell CI; the occupation numbers served as a useful guide).

Since the NSO's from the KL shell CI are orthogonal and since they match quite well their K or L counterparts, the new spin-orbital

TABLE 5

ENERGY VALUES AT DIFFERENT STAGES OF THE SEARCH FOR p ORBITALS

Wave function	Comments	Energy
$(s_1)^2(s_2)^2$	Watson's Hartree-Fock	-14.572986
$(s_1)^2(s_2)^2 + (s_2)^2 \sum_{i \neq j} (t_i t_j)^5$	K shell C.I. with Watson's NSO basis	-14.610596
	Idem with trial basis (see text)	-14.610624
$(s_1)^2(s_2)^2 + (s_1)^2 \sum_{i \neq j} (t_i t_j)^5$	L shell C.I. with Watson's NSO basis	-14.617783
	Idem with trial basis	-14.617391
$(s_1)^2(s_2)^2 + (s_2)^2 \sum_{i \neq j} (t_i t_j)^5$ $+ (s_1)^2 \sum_{i \neq j} (t_i t_j)^5$	KL shell C.I. with Watson's NSO basis	-14.651856
	Idem with trial basis	-14.651691
Full C.I. with $s_1, s_2, s_3, s_4, p_1, p_2, p_3$	125 C.I. with NSO's of KL shell C.I.	-14.657015

basis was constructed from them.

We had to decide which set of KL shell NSO's to investigate first, and we chose the NSO's from set A because it seemed more conventional to do so, and there were no other reasons to prefer either choice. In a way, set B was more interesting, regarding the procedure by means of which it had been obtained, but it seemed somewhat more risky.

With this, we concluded our search for s and p orbitals; the s_1 and s_2 orbitals were to remain the original HF ones (thanks to this, a cluster expansion analysis of our final wave function can be compared with the analysis of Watson's wave function made by Sinanoglu (34)) and the others were chosen successively from the highest occupation number, down. One can take advantage of this situation and define, for a given quantum number ℓ , the orbital number i according to the position of the orbital in Table 12. When the wave function is good, the occupation number spectrum varies little with further improvements; also, "crossings" are very rare and, for a given symmetry, the spacing is wide enough so that a unique mapping is possible between the NSO's of some good approximation to Ψ and the NSO's of a still better approximation to Ψ . It was with this expectation in mind, that we partitioned a set of Slater determinants into two sets L and L' (see Eq. (1.6)).

3.3. The Search for d Orbitals

A full CI treatment is one in which all possible configurations arising from the spin-orbital basis considered, are taken into account

(see Tables 1, 2 and 3).

We selected four s-type orbitals out of the six possible ones and three p-type orbitals out of the corresponding five. The energy of the full CI expansion in a 4s, 3p basis (94 configurations; 125 terms), was calculated (see Table 5), and the result considered very encouraging when compared with the sp-limit attained by Weiss (see Chapter IV). The truncation of the 125 CI expansion was tentatively made by using a rough eigenvector component criterion (see Table 6) which worked very well in this case.

We considered the four d orbitals of Watson, and we obtained a fifth one by a Schmidt orthogonalization of the STO's (see Eq.(2.7) and Table 4) with respect to the starting basis. Next, some configurations including d orbitals were considered, in which only s_1 , s_2 , s_3 , p_1 , p_2 and p_3 were included. All the possible combinations of the form $(s)^2(d)^2$, $(s)^2 d_w d_x$ and $s(p)^2 d$ were taken into account; only three configurations of type $s(d_w)^2 d_x$ were included (see Table 1); in this instance, as well as in later experiments, their eigenvector components were smaller than 10^{-5} and their energy contributions were negligible.

The resulting expansion contained 143 terms: the corresponding result is shown in Table 6. The natural orbitals of this wave function were calculated (see Table 12), and we selected the three d-type orbitals with highest occupation number. Incidentally, the s and p NSO's were seen to be identical with the original ones: in the latter ones, the former ones showed up with expansion coefficients equal

TABLE 6

ENERGY VALUES AT DIFFERENT STAGES OF THE SEARCH FOR d-ORBITALS

Truncated full (4s, 3p) 125 C.I.

Wave function	Comments	Energy
Only terms with eigenvector component larger than $5 \cdot 10^{-5}$	85 C.I.	-14.657015
Only terms with eigenvector component larger than 10^{-4}	72 C.I.	-14.657012
Only terms with eigenvector component larger than $4 \cdot 10^{-4}$	51 C.I.	-14.656983

Inclusion of d configurations

Wave function	Comments	Energy
(See text)	143 C.I.	-14.660139

to 0.9992 or larger; among the p-type NSO's, the corresponding coefficients were larger than 0.999963.

3.4. Final Selection of Configurations

In order to speed up the procedures, we left the s_5 , s_6 and p_4 (NSO's of the KL shell CI wave function) out of the picture. They are included now. The successive steps are best described in Table 8. All orbital expansion coefficients in terms of the STO basis are given in Table 7. An analysis of the final results is given in Chapter 4.

3.5. Computing Techniques

An IBM 709 computer was used throughout this work. All programs were written in Fortran II, using double precision arithmetic. The basic two electron integrals were calculated by means of the recurrence relations given by Roothaan et. al.⁽³⁵⁾ and stored on magnetic tape for use in future calculations. The generation of the 155×155 Hamiltonian matrix of our final wave function took twenty minutes. The eigenvalue and eigenvector were found by using a sub-routine program written by F. Prosser⁽³⁶⁾, which employs the Givens' method; it is written in single precision arithmetic, but includes selective rounding off at all the critical stages.

A computer program was written which, under certain conditions, improves an approximate eigenvalue and eigenvector to any desired accuracy. It consists of an application of the Gauss-Seidel-Lanczos⁽³⁷⁾ iteration method to the partitioning technique equations. The nodes

of the bracketing function are found by means of a direct interpolation between the value of the bracketing function for an initial energy and its value after a 45° construction⁽³⁸⁾. The bracketing function calculated at this interpolation point is usually smaller than 10^{-9} , but since this value may be in error, we calculate the final bounds for the lowest eigenvalue of the finite Hamiltonian matrix in the following way: let \tilde{E} and \tilde{c} be the approximate eigenvalue and eigenvector respectively; the residual vector η is

$$\eta = (H - \tilde{E})\tilde{c}$$

and if \tilde{c} is normalized, it may be shown that⁽⁴¹⁾

$$E = \tilde{E} \pm \|\eta\|$$

The Lanczos method consists in minimizing the residual vector after several applications of the Gauss-Seidel iterations.

The eigenvalues and eigenvectors of several Hamiltonian matrices calculated with Prosser's subroutine, were checked against the ones obtained with our own program; the eigenvalues were usually accurate to 8 figures, while the eigenvectors were correct in 3 to 7 figures.

TABLE 7

EXPANSION COEFFICIENTS a_{ji} OF THE R_{it} 's IN TERMS OF THE STO BASIS

s-type orbitals

j	s_1	s_2	s_3	s_4	s_5	s_6
1	0.4848471	-0.0811293	0.2215881	-0.7484295	-1.2618586	3.6012094
2	0.2176069	-0.1473455	0.2118045	-0.2439869	-0.6774852	1.5518720
3	0.2641661	-0.0511496	0.0881228	-0.4698174	1.0142963	-9.8829009
4	-0.2683019	1.3329118	-1.4271122	-0.6530959	1.9887342	-1.2450080
5	0.1682250	-0.0410639	-0.0703984	1.3709584	1.4541747	8.4482575
6	0.1675844	-0.3867803	0.4399173	0.0385623	-0.7955710	1.0364565
7	0.0451277	-0.0075224	0.0205954	-0.0696847	-0.1174201	0.332034
8	-0.0452875	0.2248252	1.1745532	0.6302475	-0.3754253	-0.6063636
9	0.0668827	-0.0276480	-0.1816087	0.3960528	-1.7456065	-3.4694061

p-type orbitals

j	p_1	p_2	p_3	p_4	d_1	d_2	d_3
1	-0.0002040	0.2462577	-0.3178171	0.1917032	0.0185660	0.2502715	0.1189756
2	0.5423828	0.0284567	0.5032411	1.3446407	-0.6086959	0.4169010	1.5133124
3	-0.0064305	0.0739821	-1.6860011	1.4477927	-0.0557020	-0.3503872	-2.5161285
4	-0.2041045	0.0725425	0.2090686	0.4041883	1.5457412	-0.3762812	-1.3155202
5	0.0144645	0.6971807	1.7181593	-2.1723786	0.0701806	1.0691261	2.0186191
6	0.7522239	-0.2673542	-0.7705186	-1.4896289			
7	-0.0267372	0.0095029	0.0273875	0.0529478			

TABLE 8

FINAL SELECTION OF CONFIGURATIONS FOR A BASIS OF 6s, 4p AND 3d ORBITALS

Wave function	Comments	Energy
All possible s-type and $(s)^2(p)^2$ terms	128 C.I.	-14.652625
Only terms with eigenvector component larger than $2 \cdot 10^{-4}$	47 C.I.	-14.652599
Addition of all $(s)^2 p_x p_x$ and $s_x s_x (p)^2$ terms to the 47 C.I.	143 C.I.	-14.654846
Only terms with eigenvector component larger than 10^{-4}	79 C.I.	-14.654845
Addition of all $s_1 s_1 p_x p_x$, $(p_1)^2 (p_2)^2$ and $(p_1)^2 (p_3)^2$ terms	145 C.I.	-14.659124
Only configurations where at least one term has eigenvector component larger than $2 \cdot 10^{-4}$, and all $s_2 s_2 p_x p_x$ terms	155 C.I.	-14.659132
Only configurations where at least one term has eigenvector component larger than $4 \cdot 10^{-4}$, and several configurations with d orbitals	155 C.I.	-14.662132

CHAPTER IV

ANALYSIS OF THE RESULTS

In this chapter, we shall mention first the salient features of this calculation. Then, we shall discuss how to improve it. Nothing will be said about the possibilities of obtaining comparable accuracies for larger systems, since this would be pure speculation.

4.1. Salient Features

The total energy obtained for Be ground state is the lowest one found so far by means of a rigorous calculation (see Table 9; the estimated non-relativistic energy is -14.66745 m.a.u.⁽²³⁾). The improvement over Weiss' energy value is believed to be due to the addition of more configurations containing p-type orbitals. If only s-type configurations are considered, the best energy for a wave function with these characteristics is called the s-limit energy. Weiss' s-limit energy is -14.59110 m.a.u. (see Table 9 of his paper); ours is -14.59073 m.a.u. The two energies are so close to each other that it is impossible to decide which s-type basis will be more effective in lowering the energy of the final wave function. The sp-limit of Weiss is only -14.65722 m.a.u., which compares unfavorably with ours: -14.659132 m.a.u. When adding configurations containing d-type

TABLE 9

RIGOROUS CALCULATION ON Be GROUND STATE

Year	Computer	Wave function	Energy
1960	IBM 704	37 C.I.; uses, in part, a H.F. basis, and up to g-type orbitals	-14.65740 ^a
1961	UNIVAC	55 C.I.; uses non-orthogonal basis and up to f-type orbitals. Optimizes non-linear parameters	-14.66090 ^b
1965	IBM 7074	Augmented separated pair expansion 29 terms, up to d-type orbitals. Optimizes non-linear parameters	-14.66179 ^c
1966	IBM 709	80 C.I.; uses a mixed basis of H.F. orbitals and approximate NSO's; up to d-type orbitals	-14.66203 ^d
		155 C.I.	-14.66213 ^d

^aWatson, R.E., Phys. Rev. 119, 170 (1960).

^bWeiss, A.W., Phys. Rev. 122, 1826 (1961).

^cMiller, K.J., and Ruedenberg, K., preprint, Institute for Atomic Research, Department of Chemistry, Department of Physics, Iowa State University, Ames, Iowa.

^dThis calculation.

orbitals, Weiss' improvement is of -0.00317 m.a.u.; ours is only of -0.00300 m.a.u. The improvement obtained by Watson when adding the d orbitals is just about the same. Since we did not include the important configurations of the type $(p)^2(d)^2$, it is probable that our improvement will be slightly larger than theirs, though of the same order of magnitude.

To compare our wave function with others, it would be necessary to transform all of them, including ours, into an NSO expansion form. Barnett et. al.⁽²⁶⁾ did this for Watson's and Weiss' wave functions. Since our 143 CI wave function (see the end of Section 3.3 and Table 6) is almost in natural form, it is possible to make a comparison of our expansion coefficients with those from the natural expansions given by Barnett et. al. They are very similar, all phases agree, and none of Weiss' configurations is missing from our wave function. For example, the first five coefficients of Weiss' expansion are 0.95327 , -0.29626 , -0.036491 , -0.028171 and -0.017063 , while our coefficients corresponding to the same configurations are 0.95255 , -0.29612 , -0.040428 , -0.027849 and -0.016523 , respectively. The small difference between -0.29626 and -0.29612 , which correspond to $(s_1)^2(p_1)^2$, may be due to the fact that our s_1 and p_1 are almost NSO's; it may also be a coincidence.

In Table 10, we present some features of our wave function which are of wide interest. First, the truncations made in the 155 CI wave function, illustrate the goodness of the eigenvector component criterion in this respect. The second series of truncations is relevant both to the cluster expansion and to the problem

TABLE 10

ENERGIES FOR SOME TRUNCATED EXPANSIONS

Truncations from 155 C.I.

Wave function		Energy
Only terms with eigenvector component larger than $5 \cdot 10^{-4}$	80 C.I. ^a	-14.662027
Only terms with eigenvector component larger than $8 \cdot 10^{-4}$	68 C.I. ^b	-14.661923
Only terms with eigenvector component larger than 10^{-3}	59 C.I. ^c	-14.661619

Truncations from 80 C.I.

Wave function		Energy
Triple excitations left out	68 C.I.	-14.661772
Triple and single excitations left out	63 C.I.	-14.661228
Quadruple, triple and single excitations left out	53 C.I.	-14.658293
Only (t) ² (u) ² terms	36 C.I.	-14.652744

^aSee Table 11.^bIn Table 11, terms 67 and 69 through 79 are missing.^cIn Table 11, terms 58, 59, 61 and 63 through 80 are missing.

of the convergence of the CI method itself.

We shall define the correlation energy E_{corr} as

$$E_{\text{corr}} = E_{\text{exact}}(\text{non-relativistic}) - E_{\text{HF}}(\text{non-relativistic}) .$$

A rigorous definition is given by Lowdin^(8c).

In quantitative estimations of correlation energies by the many electron theory⁽³⁹⁾ or the infinite order perturbation theory⁽⁴⁰⁾, some assumptions are made about the magnitudes of several terms appearing in the theory. To this author's knowledge, a direct check on the energy obtained has never been done. Either the average value of the obtained wave function, with respect to the Hamiltonian, can be calculated without serious approximations in the integrals, in which case the omission of an energy check is unjustified, or some mathematically correct energy bounds for this average value are not obtainable, in which case the method cannot be said to be rigorous. Tuan and Sinanoglu⁽³⁹⁾ have reported a Be ground state calculation in which 99.87 % of the correlation energy was accounted for. On the basis of an analysis of Watson's wave function⁽³⁴⁾, they assumed that the energy contributions of the single and triple excitations were negligible; we see, from Table 10, that they contribute very little, although significantly.

Our quadruply excited configurations differ slightly from those of Watson, but their energy contributions are comparable. It is not worthwhile to make a cluster expansion analysis of our wave function at this moment, since we hope to improve it in the next few months, but after that, we believe it will prove to be useful.--

In Table 11, the eigenvector of our 80 CI wave function is displayed. We note the relatively high eigenvector component of some single excitations. These are accurate to all figures shown in the table; they are written here only for the purpose of illustration, since, in order to use them in actual computations, more ciphers are needed.

In table 12, some fairly representative occupation number spectra of the wave functions mentioned here are shown. The rise of the occupation number of p_3 in the final wave function can be rationalized by noting that the inclusion of p_4 brings into the CI expansion, several configurations containing that orbital and with relatively high eigenvector component. Of course, the next thing to be done is to employ our final NSO's as a new basis, including s_1 and s_2 ; we shall consider this possibility in the next section.

We have already pointed out in Chapter III some of the uses we have made of Table 12.

In Table 13, we compare the radial density distribution of our final 155 CI wave function with those obtained by means of a HF wave function. In order to obtain the average radial density, the p-type contributions must be multiplied by 3, and the d-type ones, by 5. If one compares the average radial density, one finds that the HF is larger in the K shell region and smaller in the L shell region. As expected, the p-type contributions are essentially localized in the L shell region.

TABLE 11

AN 80 TERMS WAVE FUNCTION FOR THE GROUND STATE OF THE Be ATOM^a

Configuration ^b	Eigenvector
$(s_1)^2(s_2)^2$	0.952666
$(s_1)^2(p_1)^2$	-0.294953
$(s_1)^2(s_3)^2$	-0.039464
$(s_1)^2 s_2 s_3$ *	-0.038081
$(s_2)^2(p_2)^2$	-0.027936
$(s_2)^2(s_4)^2$	-0.017576
$(s_1)^2(d_1)^2$	-0.016772
$(s_2)^2 s_3 s_4$	0.013383
$(s_1)^2 s_2 s_4$ *	-0.008534
$(p_1)^2(p_2)^2$ (2)	-0.008491
$(s_2)^2 p_1 p_2$	-0.008306
$s_1 s_2 p_1 p_2$ (1)	0.008203
$(s_1)^2 s_3 s_4$	-0.007189
$(s_2)^2(d_2)^2$	-0.006559
$s_1 s_2 p_2 p_3$ (2)	0.006490
$s_1 s_2 p_2 p_4$ (2)	0.006082
$s_1 s_2(s_4)^2$	-0.005979
$s_1 s_2 p_1 p_3$ (1)	0.005950
$s_1 s_2(p_1)^2$	0.005668
$(s_4)^2(p_1)^2$	0.005590

TABLE 11 continued

Configuration		Eigenvector
$(s_2)^2(s_3)^2$		-0.005553
$s_1 s_2 p_1 p_2$	(2)	-0.005043
$(s_2)^2(p_3)^2$		-0.004801
$s_1 s_2 p_1 p_4$	(1)	0.004455
$s_3 s_4 (p_1)^2$		-0.004131
$s_1 s_2 s_3 s_4$	(1)	0.004062
$s_1 s_2 s_3 s_4$	(2)	-0.003636
$s_1 s_2 p_3 p_4$	(2)	0.003266
$(s_2)^2(s_5)^2$		-0.003162
$s_1 s_2 (s_3)^2$		-0.003072
$(s_1)^2(s_4)^2$		-0.002836
$s_1 s_2 (p_2)^2$		-0.002740
$(s_1)^2 s_2 s_5$	*	0.002482
$s_1 s_3 p_1 p_2$	(1) ***	0.002316
$(p_1)^2(p_2)^2$	(3)	0.002291
$s_1 s_2 p_3 p_4$	(1)	0.002271
$s_2 s_4 (p_1)^2$	***	0.002178
$s_1 s_2 p_2 p_3$	(1)	0.002131
$(s_2)^2(d_3)^2$		-0.002044
$(p_1)^3 p_2$		0.001946
$(s_3)^2(p_1)^2$		0.001927
$(s_1)^2(p_4)^2$		-0.001872

TABLE 11 continued

Configuration		Eigenvector
$(s_2)^2 p_1 p_3$		-0.001793
$(s_1)^2 p_3 p_4$		-0.001787
$s_1 s_2 (p_4)^2$		0.001647
$s_1 s_2 (p_3)^2$		0.001608
$(p_1)^2 (p_3)^2$	(2)	-0.001593
$(s_2)^2 (p_4)^2$		-0.001576
$s_1 s_2 p_1 p_4$	(2)	0.001544
$s_2 s_3 (p_1)^2$	***	-0.001464
$s_1 s_4 p_1 p_2$	(1) ***	-0.001355
$(s_2)^2 p_2 p_4$		0.001180
$s_1 s_3 p_1 p_3$	(1) ***	-0.001171
$(s_2)^2 s_3 s_5$		-0.001145
$(s_3)^2 (p_2)^2$		0.001136
$(s_2)^2 (p_1)^2$		-0.001124
$s_2 s_3 (p_2)^2$	***	0.001094
$s_1 s_2 (s_5)^2$		-0.001056
$(s_1)^2 (p_3)^2$		-0.001049
$s_1 s_2 p_2 p_4$	(1)	0.001037
$(s_5)^2 (p_1)^2$		0.001033
$(s_1)^2 s_4 s_5$		0.001020
$s_1 (p_1)^2 d_1$	***	0.000877
$(s_3)^2 (s_4)^2$		0.000862
$(s_2)^2 (s_6)^2$		-0.000848

TABLE 11 continued

Configuration		Eigenvector
$s_1 s_2 s_3 s_5$	(1)	-0.000818
$s_2 (s_3)^2 s_4$	***	-0.000793
$s_1 s_3 (p_1)^2$	***	0.000791
$(s_2)^2 s_4 s_5$		-0.000762
$s_2 s_3 (s_4)^2$	***	0.000730
$s_1 s_2 s_4 s_5$	(1)	0.000716
$s_1 s_3 p_1 p_4$	(1) ***	0.000675
$s_1 s_5 p_1 p_2$	(2) ***	0.000609
$(s_1)^2 p_1 p_2$		0.000602
$(p_1)^4$		0.000599
$(s_1)^2 s_2 s_6$	*	0.000586
$s_1 (s_2)^2 s_3$	*	0.000549
$(s_2)^2 p_1 p_4$		-0.000541
$s_1 s_2 s_3 s_5$	(2)	0.000528
$(s_1)^2 (s_5)^2$		-0.000524

a

The energy corresponding to this wave function is $E = -14.662027$ a.u.

b

The number in parenthesis indicates which term of the degenerate configuration is used. The asterisk (*) denotes a singly excited configuration; three asterisks (***), a triple excitation.

TABLE 12

OCCUPATION NUMBER SPECTRA OF SOME GROUND STATE Be WAVE FUNCTIONS

	Weiss ^a	Watson ^a	K shell CI ^b	L shell CI ^b	KL shell CI ^b	143 CI ^c	Final ^d
s ₁	0.998324	0.998306	0.998421 ₃₂	1.000000	0.998566 ₉	0.998303	0.998218
s ₂	0.910279	0.918574	1.000000 ₀	0.903810 ₁₀₉₅₇	0.917428 ₂₃₀₈₉	0.910003	0.910450
p ₁	0.087956	0.081101		0.094515 ₈₇₂₈₄	0.080974 ₇₅₂₂₉	0.087954	0.087493
s ₃	0.001644	0.000721		0.001660 ₇₄₁	0.001709 ₈₂₄	0.001864	0.001841
p ₂	0.000916	0.000842		0.000006 ₁₇	0.000831 ₂₂	0.000956	0.000990
s ₄	0.000463	0.000034		0.000008 ₁₆	0.000439 ₁₈	0.000528	0.000531
d ₁	0.000293	0.000332				0.000274	0.000284
p ₃	0.000037	0.000023	0.000031 ₂₉	0.0000006 ₁	0.000029 ₅	0.000044	0.000108
d ₂	0.000045	0.000041				0.000043	0.000043
p ₄	0.000018	0.000001			0.000010 ₀₃		0.000021

TABLE 12 continued

Weiss	Watson	K shell CI	L shell CI	KL shell CI	1 $\frac{1}{2}$ CI	Final
s ₅	0.000012	0.000009	0.0000004 ₄	0.000012 ₆		0.000015
d ₃	0.000003	0.000003			0.000004	0.000004
s ₆	0.000001	0.000007	0.0000007 ₆	0.0000008 ₄₀		0.0000008

^a See Ref. 26 in text.

^b See Table 5.

^c See Table 6.

^d See Table 8.

TABLE 13

RADIAL DENSITY PROBABILITY DISTRIBUTION

Hartree-Fock ^a		Final wave function		
r(a.u.)		s-type	p-type	d-type
0	0	0	0	0
0.01	0.02053	0.02055	0.00000	0.00000
0.02	0.07582	0.07587	0.00000	0.00000
0.03	0.15754	0.15756	0.00000	0.00000
0.04	0.25869	0.25862	0.00000	0.00000
0.05	0.37343	0.37319	0.00001	0.00000
0.06		0.49644	0.00001	0.00000
0.07		0.62437	0.00002	0.00000
0.08		0.75372	0.00003	0.00000
0.09		0.88185	0.00004	0.00000
0.10	1.00818	1.00667	0.00006	0.00000
0.12		1.24016	0.00010	0.00000
0.14		1.44520	0.00015	0.00000
0.16		1.61726	0.00022	0.00000
0.18		1.75486	0.00030	0.00000
0.20	1.86205	1.85859	0.00038	0.00001
0.25	1.98872	1.98449	0.00062	0.00001
0.30	1.96401	1.95911	0.00085	0.00002
0.35	1.83867	1.83344	0.00106	0.00002
0.40	1.65609	1.65106	0.00123	0.00002
0.45	1.44901	1.44468	0.00138	0.00002
0.50	1.24002	1.23675	0.00153	0.00002
0.60	0.86751	0.86646	0.00189	0.00001
0.70	0.58938	0.58945	0.00244	0.00001
0.80	0.40662	0.40634	0.00319	0.00000
0.90	0.30138	0.29967	0.00407	0.00000
1.00	0.25213	0.24849	0.00502	0.00000
1.10	0.23991	0.23419	0.00597	0.00000
1.20	0.25001	0.24219	0.00690	0.00001
1.30	0.27188	0.26197	0.00776	0.00001
1.40	0.29838	0.28634	0.00855	0.00001
1.50	0.32489	0.31071	0.00925	0.00001
1.60	0.34862	0.33233	0.00985	0.00002
1.70	0.36803	0.34972	0.01036	0.00002
1.80	0.38243	0.36224	0.01076	0.00003
1.90	0.39168	0.36982	0.01105	0.00003
2.00	0.39599	0.37268	0.01124	0.00003
2.20	0.39156	0.36610	0.01130	0.00003
2.40	0.37346	0.34675	0.01098	0.00003
2.60	0.34615	0.31897	0.01035	0.00003

TABLE 13 continued

r(a.u.)	Hartree-Fock	Final wave function		
		s-type	p-type	d-type
2.80	0.31357	0.28653	0.00948	0.00002
3.00	0.27878	0.25237	0.00846	0.00002
3.20	0.24401	0.21864	0.00738	0.00002
3.40	0.21078	0.18679	0.00630	0.00001
3.60	0.18006	0.15679	0.00526	0.00001
3.80	0.15231	0.13177	0.00432	0.00001
4.00	0.12775	0.10915	0.00348	0.00000
4.20	0.10635	0.08972	0.00277	0.00000
4.40	0.08794	0.07327	0.00216	0.00000
4.60	0.07227	0.05949	0.00167	0.00000
4.80	0.05908	0.04806	0.00127	0.00000
5.00	0.04806	0.03866	0.00096	0.00000
5.50		0.02207	0.00045	0.00000
6.00	0.01611	0.01238	0.00020	0.00000
6.50		0.00684	0.00008	0.00000
7.00	0.00500	0.00374	0.00003	0.00000
7.50		0.00202	0.00001	0.00000

^a C. C. J. Roothaan, L. M. Sachs and A. W. Weiss, Rev. Mod. Phys. 32, 186 (1960).

4.2. Possible Improvements

The 80 CI wave function (see Table 10), constitutes a starting point for obtaining better approximations. The first thing we plan to do, even before making an orbital exponent variation, is to compute the energy of the 80 CI wave function in the new NSO basis. We believe that it makes sense to introduce the s_1 and s_2 NSO's from our final wave function, as suggested by an analysis of Table 14, where the results of a $c_1(s_1)^2(s_2)^2 + c_2(s_1)^2(p_1)^2$ wave function are displayed. In this table, the best of Watson's results shows a relatively high energy for the ground configuration, which is almost identical with the energy of $(s_1)^2(s_2)^2$ when s_1 and s_2 are taken to be the two NSO's of highest occupation number of the KL shell CI wave function (our value is -14.57235; see also Section 3.2). At the time we found this result, we were not aware of Watson's, and very much in favor of a HF basis.

After this is done, we intend to modify the STO basis in the light of the results shown in Table 13. At the same time, an enlargement of the STO basis is felt to be necessary. With a basis of s, p and d orbitals, it should be possible to get an energy close to that of Kelly⁽⁴⁰⁾. Only then do we intend to add higher symmetry type orbitals. Of course, configurations like $(p)^2(d)^2$, which have been omitted in this study, will be included.

Although this work is not completed, it seems reasonable to expect that further significant improvement can be achieved, and we are optimistic.

TABLE 14

2 CI WAVE FUNCTIONS FOR Be GROUND STATE

Wave function	$(1s)^2(2s)^2$ energy	2 CI energy
Application of Veillard's 2 CI, SCF formalism	-14.572907	-14.615449 ^a
1s, 2s: Watson's HF ^b : NSO of the KL shell CI	-14.572986	-14.615797 ^c
1s, 2s: HF 2p from 2 CI, SCF	-14.57301	-14.61594 ^d
2 CI, SCF	-14.57234	-14.61652 ^d

^aE. Clementi and A. Veillard, J. Chem. Phys. 44, 3051 (1966)^bR. E. Watson, Phys. Rev. 119, 170 (1960)^cThis calculation^dR. E. Watson, Ann. Phys. (N.Y.), 13, 250 (1961)

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BIOGRAPHICAL SKETCH

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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